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THE EXCESS ENTHALPIES OF CYCLOOCTANE + *n*-ALKANES

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ABSTRACT

The excess enthalpies of cyclooctane + *n*-hexane, + *n*-heptane, + *n*-octane, + *n*-dodecane and + *n*-hexadecane have been measured over the whole composition range at two temperatures. The results, together with previously published excess volume results, have been fitted to the Flory theory of liquid mixtures.

INTRODUCTION

The molar excess volumes (V_m^E) of cyclooctane with an *n*-alkane have recently been reported by the authors [1,2]. In this work, we present the molar excess enthalpies (H_m^E) of the same mixtures at two temperatures. The H_m^E results at 25°C presented in this work, together with the previously reported V_m^E results at 25°C have been used to test the Flory theory of liquid mixtures.

EXPERIMENTAL

The purification procedures for all the hydrocarbons have been described [3] as has the method for determining H_m^E using the LKB 2107 microcalorimeter [3].

TABLE 1

Molar excess enthalpy H_m^E for x c-C_8H_{16} $+(1-x)$ n-C_{y+2} and the deviations δH_m^E calculated from eqn. (1) and Table 2

x	H_m^E (J mole^{-1})	δH_m^E (J mole^{-1})	x	H_m^E (J mole^{-1})	δH_m^E (J mole^{-1})	x	H_m^E (J mole^{-1})	δH_m^E (J mole^{-1})
n-C_6H_{14} at 15°C								
0.1285	77.9	−0.3	0.4951	214.9	−0.2	0.6788	212.8	1.8
0.2522	143.6	1.6	0.5957	219.8	−0.5	0.7503	190.4	−0.6
0.3708	186.3	−1.0	0.6117	219.7	0.1	0.8786	121.0	−0.1
0.4480	206.3	−0.8						
n-C_6H_{14} at 25°C								
0.0768	48.0	0.7	0.4217	191.6	0.6	0.6675	200.2	−0.4
0.1526	87.1	−2.1	0.4489	196.4	−0.2	0.7881	164.1	−0.6
0.2620	140.3	0.1	0.4972	204.9	1.2	0.8442	134.6	−0.9
0.3933	184.7	0.5	0.5860	208.8	0.6	0.9173	83.7	0.5
$n0C_7H_{16}$ at 15°C								
0.140	97.5	1.2	0.5136	247.9	2.5	0.6977	236.8	−3.0
0.2624	158.2	−4.0	0.5755	253.5	2.3	0.8061	194.3	−2.6
0.3894	213.8	−1.2	0.6254	251.0	0.5	0.8828	142.5	1.3
0.4776	241.8	.8						
2108								
n-C_7H_{16} at 25°C								
0.1159	75.0	−0.1	0.3981	200.2	−3.1	0.7598	198.9	−0.3
0.1392	90.6	1.1	0.5069	226.5	3.6	0.7860	186.4	−2.9
0.1692	106.8	−0.4	0.5169	226.2	2.3	0.8034	178.5	−3.1
0.3068	171.5	−2.5	0.6374	227.9	3.5	0.8872	130.9	1.9
n-C_8H_{18} at 15°C								
2108								
0.1493	109.5	0.2	0.4875	270.3	1.3	0.7035	260.0	−1.9
0.2827	194.1	−0.5	0.5337	276.3	1.0	0.7782	232.5	−1.0
0.3362	221.8	0.5	0.5846	279.0	1.4	0.8933	148.8	0.3
0.4078	246.2	−2.7	0.6475	274.5	1.2			

n-C_8H_{18} *at 25°C*								
0.0922	65.1	−0.8	0.4224	225.3	−2.1	0.7537	232.6	3.5
0.1601	110.1	0.5	0.5264	248.0	−1.3	0.7820	217.2	0.1
0.2358	155.1	2.8	0.5534	252.5	0.1	0.8552	172.3	0.2
0.2743	172.0	0.6	0.5806	253.2	−1.0	0.1955	115.5	−0.6
0.4021	220.4	−1.0	0.6573	250.9	−0.8			
n-$C_{12}H_{26}$ *at 15°C*								
2108								
0.1273	132.2	0.6	0.4910	372.6	−0.6	0.7754	339.8	0.6
0.2798	260.1	−3.2	0.5703	392.3	3.1	0.8309	289.6	−3.0
0.3537	312.9	0.6	0.6167	392.8	2.0	0.9209	171.7	0.8
0.4015	338.4	0.4	0.7265	364.6	−1.6			
n-$C_{12}H_{26}$ *at 25°C*								
2108								
0.1166	112.0	0.0	0.4598	331.0	1.8	0.7289	338.4	1.1
0.2183	195.8	0.5	0.4811	338.6	2.4	0.8074	291.9	0.4
0.2281	201.2	−1.3	0.5392	351.6	0.8	0.8754	225.6	2.5
0.2894	245.8	1.2	0.6187	355.4	−2.8	0.9204	154.3	−4.8
0.4078	305.8	−2.5	0.6317	355.6	−2.2	0.9299	146.4	2.9
2108								
n-$C_{16}H_{34}$ *at 25°C*								
2108								
0.1522	178.6	0.6	0.4746	431.8	4.5	0.7154	438.2	−1.3
0.2385	265.9	−0.9	0.5574	453.0	1.1	0.7651	413.2	0.1
0.3550	359.5	−2.5	0.6269	456.4	−1.1	0.8628	312.5	0.1
0.4123	397.2	−0.3	0.6655	453.4	−0.2	0.9360	177.3	0.1
n-$C_{16}H_{34}$ *at 35°C*								
2108								
0.1022	102.3	−0.4	0.4690	355.4	2.5	0.6762	382.0	−0.8
0.1735	168.7	2.9	0.5662	382.7	0.9	0.7451	357.4	−2.2
0.2336	214.2	−1.7	0.5890	384.5	−0.6	0.7976	328.2	2.5
0.2366	234.5	−3.1	0.6294	386.2	−1.1	0.9358	144.2	−1.2
0.3627	301.4	1.3						

RESULTS

The H_m^E results are given in Table 1 together with the deviations δH_m^E calculated from the smoothing equation

$$\delta H_m^E = H_m^E - x(1-x)\sum_{r=0}^{r} A_r(1-2x)^r \tag{1}$$

where x denotes mole fraction. The value of the coefficients A_r are given in Table 2.

DISCUSSION

Although H_m^E for other systems of the type cycloalkane + an n-alkane have been reported by other workers, no H_m^E measurements for cyclooctane + n-alkane mixtures have been previously reported.

The H_m^E results presented here are very similar to the H_m^E results for cyclohexane + n-alkane mixtures [4–8] but are less positive by amounts which vary from 12 J mole^{-1} for n-hexane to 66 J mole^{-1} for n-hexadecane systems. These values refer to mixtures studied at 25°C and at compositions of 0.5 mole fraction. Again, as in the case of cyclohexane + n-alkane mixtures [7–9], H_m^E and the magnitude of $\partial(H_m^E/\partial T)_{x=0.5}$ increases with increasing carbon number.

The properties of the pure substances such as density (ρ), coefficients of thermal expansion (α) and the isothermal compressibility (κ) required for

TABLE 2

Smoothing coefficients for x c-C_8H_{16} + $(1-x)$ n-C_yH_{2y+2} at temperatures T determined from the results of Table 1

n-Alkane	T (°C)	A_0 (J mole^{-1})	A_1 (J mole^{-1})	A_2 (J mole^{-1})	A_3 (J mole^{-1})
C_6H_{14}	15	862.9	−251.2	91.1	−68.0
C_6H_{14}	25	816.1	−226.1	94.8	−43.6
C_7H_{16}	15	972.8	−339.6	158.8	−84.9
C_7H_{16}	25	888.4	−226.6	202.2	−222.1
C_8H_{18}	15	1084.2	−310.6	167.7	−256.6
C_8H_{18}	25	981.3	−348.4	233.7	−119.7
$C_{12}H_{26}$	15	1503.4	−548.9	337.2	−235.4
$C_{12}H_{26}$	25	1366.8	−546.0	357.5	−157.9
$C_{16}H_{34}$	25	1746.8	−677.9	481.8	−383.6
$C_{16}H_{34}$	35	1457.2	−678.6	389.6	−87.0

TABLE 3

Properties of pure substances at 25°C

Hydrocarbon	ρ (g cm^{-3})	Ref.	$10^3\alpha$ (K^{-1})	Ref.	$10^{12}\kappa$ (Pa)$^{-1}$	Ref.
C_8H_{16}	0.83151	10	0.979	11	803	11
C_6H_{14}	0.65481	10	1.375	12	1669	12
C_7H_{16}	0.67951	10	1.245	12	1438	12
C_8H_{18}	0.69849	10	1.150	12	1282	12
$C_{12}H_{26}$	0.74516	10	0.970	12	988	12
$C_{16}H_{34}$	0.76996	10	0.898	12	857	12

the Flory theory, are given in Table 3. Also required for the Flory theory are the V_m^E data on the same systems. This data is summarised in Table 4 by the coefficients B_r from the smoothing equation

$$\delta V_m^E = V_m^E - x(1-x)\sum_{r=0}^{r} B_r(1-2x)^r \tag{2}$$

given in refs. 1 and 2.

The Flory theory [13,14] used in this treatment has been used by Benson et al. [15,16] for decalin + cycloalkanes. We have used an identical approach and have assumed

$$\frac{S_1}{S_2} = \left(\frac{V_1^*}{V_2^*}\right)^{1/3}$$

We did not, however, consider S_1/S_2 to be an adjustable parameter.

In this work, we have determined $\chi_{12}(H_m^E)$ from H_m^E at all compositions between 0 and 1.0 at 0.01 mole fraction intervals. The value of $\chi_{12}(H_m^E)$

TABLE 4

Smoothing coefficients, B_r, from eqn. (2) for x c-C_8H_{16} + $(1-x)$ n-C_yH_{2y+2} at 25°C taken from refs. 1 and 2

n-Alkane	B_0 (cm^3 mole^{-1})	B_1 (cm^3 mole^{-1})	B_2 (cm^3 mole^{-1})	B_3 (cm^3 mole^{-1})	Ref.
C_6H_{14}	−1.975	−0.868	−0.011	0.315	2
C_7H_{16}	−0.783	−0.895	−0.220	0	1
C_8H_{18}	−0.181	−0.525	0.349	0	1
$C_{12}H_{26}$	1.423	−0.764	0.308	0	1
$C_{16}H_{34}$	2.321	−1.049	0.256	0	1

TABLE 5

The results of fitting the Flory theory to the mixtures x c-$C_8H_{16}+(1-x)$ n-C_yH_{2y+2}

n-Alkane	$10^7\ \chi_{12}(H_m^E)$ (J m^{-3})	$\sigma(H_m^E)$ (J mole^{-1})	$\sigma^*(V_m^E)$ (cm^3 mole^{-1})	$10^7\ \chi_{12}(V_m^E)$ (J m^{-3})	$\sigma(V_m^E)$ (cm^3 mole^{-1})	$\sigma^*(H_m^E)$ (J mole^{-1})
C_6H_{14}	0.863	17.7	0.057	1.137	0.030	58.9
C_7H_{16}	0.852	20.9	0.087	1.211	0.063	80.7
C_8H_{18}	0.872	24.4	0.069	1.180	0.044	69.9
$C_{12}H_{26}$	1.075	26.2	0.089	1.513	0.046	109.8
$C_{16}H_{34}$	1.290	25.6	0.143	2.086	0.034	212.1

which minimised the standard deviation of $\sigma(H_m^E)$ was then determined. $\sigma(H_m^E)$ was calculated from

$$\sigma(H_m^E)^2 = \sum_{i=1}^{98} \left[H_{m,exp}^E(x_i) - H_{m,calc}^E(x_i)\right]^2/97 \tag{3}$$

Using $\chi_{12}(H_m^E)$, the predicted value of excess molar volumes ($V_{m,calc}^E$) were calculated and $\sigma^*(H_m^E)$ computed using a similar equation to eqn. (3). The values of $\chi_{12}(H_m^E)$, $\sigma(H_m^E)$ and $\sigma^*(V_m^E)$ are given in columns 2–4 of Table 5.

In addition, we have reversed the procedure and determined $\chi_{12}(V_m^E)$ from the V_m^E smoothing coefficients of Table 4 and hence determined $\sigma(V_m^E)$ and $\sigma^*(H_m^E)$. The results are given in columns 5–7 of Table 5.

Judging from the standard deviation results of Table 5, the Flory one-parameter equation provides a reasonable fit for both H_m^E and V_m^E data. More important, however, is the predictive power of the Flory theory. The standard deviations $\sigma^*(V_m^E)$, calculated from $V_{m,calc}^E$, which in turn was determined from experimental H_m^E data, are given in Table 5. The values of $\sigma^*(V_m^E)$ for the mixtures cyclooctane + *n*-hexane, + *n*-heptane, + *n*-octane and + *n*-dodecane are less than 0.09 cm^3 $mole^{-1}$. This is remarkable when considering that the theory contains only one parameter and that only H_m^E data was used to predict V_m^E.

The result for the *n*-hexadecane systems is not as good and is very likely due to the disparity in size between the cyclooctane and the *n*-hexadecane.

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REFERENCES

1 T.M. Letcher and W.L. Spiteri, J. Chem. Thermodyn., 11 (1979) 435.
2 T.M. Letcher, unpublished results.
3 T.M. Letcher and B.W.H. Scoones, J. Chem. Thermodyn., in press.
4 K.N. Marsh and R.D. Stokes, J. Chem. Thermodyn., 1 (1969) 223.
5 F. Vesely, Collect. Czech. Chem. Commun., 36 (1971) 2881.
6 T.L. Vinh, P. Picker, D. Patterson and P. Tancrede, J. Chem. Soc. Faraday Trans. 2, 70 (1974) 1465.
7 S.K. Yang and J.D. Gomez-Ibanez, J. Chem. Thermodyn., 8 (1976) 209.
8 G.W. Lundberg, J. Chem. Eng. Data, 9 (1964) 193.
9 M.B. Ewing and K.N. Marsh, J. Chem. Thermodyn., 2 (1970) 295.

10 F.D. Rossini, Selected Values of Physical Thermodynamic Properties of Hydrocarbons and Related Compounds, A.P.I. Research Project 44, Carnegie Press, Pittsburg, 1967.
11 M.B. Ewing and K.N. Marsh, J. Chem. Thermodyn., 9 (1977) 371.
12 M. Diáz Peña and G. Tardajos, J. Chem. Thermodyn., 10 (1978) 19.
13 P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1833.
14 A. Abe and P.J. Flory, J. Am. Chem. Soc., 87 (1965) 1838.
15 G.C. Benson, S. Murakami, V.T. Lam and J. Singh, Can. J. Chem., 48 (1970) 211.
16 D.E.G. Jones, I.A. Weeks and G.C. Benson, Can. J. Chem., 49 (1971) 2481.